

Hydrate Phase Equilibria of the Binary Guest Mixtures Containing CO₂ and N₂

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ABSTRACT

The three-phase, hydrate-water-rich liquid-vapor (HLV), equilibria of the binary guest mixtures containing CO₂ and N₂ were determined at the temperature range of 272 to 275 K and different compositions of vapor phase. In addition, two phase equilibria of hydrate and vapor were also measured at three isothermal conditions of 274, 277 and 278 K. The resulting P-x diagram indicates that CO₂ can be more contained than N₂ in the hydrate phase. More than 96 mol % CO₂ in the mixed hydrate phase was possibly obtained from a gas mixture of 17 mol % CO₂ and 83 mol % of N₂ at 274 K. The addition of Tetrahydrofuran (THF) as a hydrate promoter extended hydrate stability region by elevating equilibrium dissociation temperature and lowering pressure. The overall hydrate equilibrium results were found to agree well with the calculated ones.

Keywords: Solid-liquid-vapor equilibria; Gas hydrate; Carbon dioxide; Nitrogen; Tetrahydrofuran; Model

INTRODUCTION

Gas hydrates are non-stoichiometric inclusion compounds formed by a lattice of water molecules, “host”, strongly hydrogen bonded, which encage low molecular weight gases or volatile liquids, “guest”, in different cavities under appropriate conditions where the low temperature and high pressure surroundings favor hydrate formation. Although guest molecules are physically enclosed within the lattice, no actual chemical union exists between the guest and host molecules. In general, several types of polyhedral cavity structures can be formed depending on the size and chemical properties of guest molecules. These structures are further arranged into the well-defined three-dimensional crystalline solids.

The hydrates of the various gases may have structures corresponding to the fundamental types of structure I (S_I) and II (S_{II}) [1]. Mixtures containing more than one gas component can similarly form a hydrate structure of one kind, but it is possible that the hydrates of the individual constituents are characterized by different structures. If a system containing only one type of hydrate is formed, the phenomenon corresponding to complete mixing of the solid solution is manifested, and thus a mixed hydrate is formed. In this study, the CO_2+N_2 mixed hydrate system would be investigated in detail. The pressure and temperature ranges of hydrate stability region were carefully determined through phase equilibrium measurements of the ternary CO_2+N_2 +water system that is considered a simplified flue gas because the main components of flue gas become CO_2 , N_2 and O_2 after a suitable pretreatment method. General characteristics of N_2 and O_2 for gas hydrates are nearly similar [2]. A conceptual CO_2 separation process from flue gas will be organized on the basis of these equilibrium data. In addition, THF was used as a hydrate promoter that can greatly reduce the required hydrate formation

pressure and enhance the corresponding kinetic rate. Cyclic ethers have been generally known to form simple hydrates with water or mixed hydrates with low-molecular weight gases such as CO_2 , CH_4 and N_2 [1]. In particular, THF forms S_{II} hydrate in which THF molecules occupy only the larger cages in the hydrate lattice. The hydrate phase behavior of the binary THF and water system can be found from Callanan and Sloan [3]. The HLV equilibria can be predicted by the statistical thermodynamic model calculation. The Soave-Redlich-Kwong equation of state (SRK-EOS) incorporated with the modified Huron-Vidal second-order mixing rule (MHV2) was adopted in this study. Details about this model calculation can be found in our previous work [4].

EXPERIMENTAL

Apparatus and Materials

A schematic diagram of the experimental apparatus used in this work is illustrated in Figure 1. The apparatus was constructed to measure the gas hydrate dissociation pressures and analyze the equilibrium compositions of all the coexisting phases via an on-line gas chromatograph. An equilibrium cell was made of stainless steel and has an internal volume of about 70 cm^3 . Two sapphire sight glasses were equipped at the front and back of the cylindrically shaped cell, and allowed visual observation of phase transitions. The cell contents were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell in the bath that contained about 30 L of ethylene glycol and water mixture. Its temperature was controlled by an externally circulating refrigerator/heater. The actual temperature in the cell was measured by a K-type thermocouple probe with a digital thermometer (Barnant Co.) of which resolution was $\pm 0.1 \text{ K}$. A Heise high pressure gauge (Dresser Industries, CMM 104957) was used

to measure the cell pressure within a maximum error of ± 0.1 bar. For measurements of vapor and liquid phase compositions at a given equilibrium condition two sampling valves (Reodyne Inc., Model 7410 and 7413) having loop volumes of 5 and 0.5 μL were installed and connected to a gas chromatograph (Hewlett-Packard, HP5890) via on-line through a high pressure metering pump (Milton Roy, 2396-31). In particular, a careful procedure was made to analyze the compositions of solid hydrates existing with other phases at equilibrium. At a specific temperature and pressure, a hydrate sampling tube directly connected to the equilibrium cell was completely evacuated by a vacuum pump. When the connection valve equipped between the tube and cell was open, a desired amount of hydrates was placed and dissociated in the tube. The dissociated gas constituents were then introduced into a gas chromatograph by a syringe injection.

Gaseous mixtures composed of the high-purity CO_2 and N_2 (over 99.99 mol%) were prepared by using two microsyringe pumps (ISCO, 260 D) having an isometric function of constant flow rate. CO_2 was initially charged to a reservoir with a predetermined amount of moles using one syringe pump and then N_2 using another syringe pump. The prepared gaseous mixtures were analyzed using a gas chromatograph for confirmation.

Procedure

After the equilibrium cell was well cleaned, the overall inner parts were evacuated with vacuum pump. An amount of approximately 50 cm^3 of water or aqueous solution containing THF was initially charged into the cell. At first, the cell was pressurized to the desired pressure with the predetermined gaseous mixture. Once the cell temperature was kept constant, hydrate nucleation was then induced by agitation of the magnetic spin bar. When gas hydrates formed and the system pressure reached a steady state, the external heater was used to increase the temperature at a rate of 1 to 2 K per hour to a

condition where the hydrate phase was dissociated and in coexistence with liquid and vapor phases. The nucleation and dissociation steps were repeated at least twice in order to remove the possibility of hysteresis effect. When the amount of minute crystals and system pressure were kept constant at least for 8 to 10 hour, the pressure was considered to be the hydrate equilibrium dissociation pressure at the specific temperature. In measuring the equilibrium compositions, the experiments need to be more carefully carried out. When the system temperature and pressure was in equilibrium, the vapor phase was analyzed at least five times through gas chromatograph. The average value was then taken as an equilibrium vapor-phase composition. On the other hand, the corresponding hydrate phase compositions were measured when the hydrate phase was in coexistence with the vapor phase. Two phases of solid hydrate and vapor can only appear either below the equilibrium temperature or above the equilibrium pressure of the HLV phases.

RESULTS AND DISCUSSION

The three phases HLV equilibria of the ternary $\text{CO}_2+\text{N}_2+\text{water}$ system were determined at several different ratios of CO_2 and N_2 . The mixed hydrates formed over the wide temperature and pressure ranges of 272-282 K and 15-300 bar largely depending on the gas-phase compositions. The measured equilibrium data were listed in Table 1 and also demonstrated in Figure 2. As simple hydrates, CO_2 and N_2 form S_I and S_{II} , respectively. The mixed hydrate structure is considered to be either S_I or S_{II} depending on the relative ratio of these two different gas molecules occupied in the small and large cavities. As generally expected, all the hydrate formation lines were located between two pure CO_2 and N_2 HLV lines, and the overall experimental data were well predicted by the

statistical thermodynamic model proposed in our previous work [4]. According to the literature [5], 85 mol % of CO₂ gaseous mixture was known as the boundary of coexisting S_I and S_{II} hydrate. In the present work, the coexistence boundary was found to be 83.7 mol % of CO₂. While the relative amount of N₂ to CO₂ increases in the gas mixture, the HLV equilibrium lines were shifted to higher pressure and lower temperature domain. As clearly seen in Figure 2, the slopes of the HLV equilibrium lines for both 6.63 and 11.59 mol % CO₂ in gaseous mixture appeared to be almost same to that of pure N₂, which confirms that S_{II} hydrates formed. However, the HLV results of 96.59 mol % CO₂ showed a small promotion effect on the HLV equilibria of pure CO₂. This phenomenon might be caused from the fact that smaller N₂ molecules occupied empty cages that could not be filled with larger CO₂ molecules. But, when the relative mol % N₂ in the binary gas mixture increases, two species might compete with each other for cage occupancy resulting in no promotion.

After close examination of equilibrium temperature and pressure behavior shown in Figure 2, three isotherms of 274, 277 and 280 K were particularly chosen. Two phase equilibria of hydrate and vapor for the ternary CO₂+N₂+water system were determined at these temperatures in order to produce the *P*-*x* diagram and the complete data were listed in Table 2 and presented in Figure 3 along with the calculated results. The proposed model was successfully applied to the *P*-*x* as well as *P*-*T* equilibrium relationships. The relative CO₂ amount in the hydrate phase increased when that in the vapor phase increased. At a fixed vapor composition of 15 mol % CO₂ the corresponding CO₂ composition in the hydrate phase at 274, 277 and 280 K appeared to be about 56, 47 and 36 mol %, respectively. It might be worthy to note from this result that the CO₂ selectivity in the hydrate phase increases when the hydrate formation

temperature lowers. Another sample of 17 mol % CO_2 in the vapor phase shows a similar trend resulting to a little higher selectivity of 58 mol % CO_2 in the hydrate phase at 274 K. Figure 2 also suggests the possibility of CO_2 separation process using hydrate formation. The total amount of gas components captured in the hydrate phase can be dissociated and easily recovered simply by either elevating temperature or decreasing pressure. Only two consecutive steps are expected to achieve the recovery of more than 95 mol % CO_2 according to Figure 3.

According to Figure 2, the mixed gas having concentrations of 17 mol % CO_2 and 83 mol % N_2 can form hydrates with water slightly above 70 bar in the case that the hydrate-dissociation temperature maintains at 273 K. However, such a high pressure requirement might be regarded as a fatal disadvantage when adopted to the actual CO_2 separation process. Therefore, the more favorable condition is to lower pressure and raise temperature much higher than 273 K for hydrate formation. But, as shown in Figure 2, when the hydrate formation temperature increases, the corresponding equilibrium pressure also increases. To solve this inherent problem, a hydrate promoter can be used to enable the operating conditions to shift to the milder one. In this study, we used THF as a potential hydrate promoter and the promotion effect of THF on the mixed hydrate formation temperature and pressure was closely examined and the overall results were given in Table 3 and Figure 4. Aqueous solutions containing 1 and 3 mol % of THF were used to form the mixed CO_2 and N_2 hydrates. As shown in this figure, a remarkable decrease of equilibrium dissociation pressure was observed for the entire temperature range. The equilibrium hydrate formation pressure under the gas compositions of 17 mol % CO_2 and 83 mol % N_2 was abruptly shifted from 83.5 bar to 4.75 bar at 275 K when 1 mol % of THF is added in the aqueous solution. When

aqueous solution containing THF is used to form the mixed gas hydrate of CO₂ and N₂, more favorable condition can be attained resulting to lowering pressure and elevating temperature. The addition of a small amount of THF to water expanded hydrate stability region, but it must be carefully noted that the promotion effect of THF shifts to inhibition effect at a certain composition. Similar results were found by Jager et al. [6] in the CH₄+1,4-dioxane+water system. Addition of 1,4-dioxane to water up to 6 mol % showed promotion effect, which was the stoichiometric ratio of S_{II} 1,4-dioxane hydrate (1/17). THF also forms S_{II} hydrate and have the same guest / host ratio to 1,4-dioxane hydrate. All lines in Figure 4 were obtained from model calculations and well agreed to the experimental data. These mixtures form S_{II} hydrate and THF molecules occupy only large cavities of the structure. Owing to relatively high vapor pressure of THF, a rigorous flash calculation was performed by using the modified UNIFAC, SRK-EOS and MHV2. For the reasonable description of hydrate phase the classical van der Waals and Platteeuw theory was adopted. The resulting optimized Kihara potential parameters are listed in Table 4. The needed parameters of pure CO₂ and N₂ were regressed from the HLV literature [1] data of simple hydrate and those of THF were obtained from the similar procedure of Jager et al. [6].

CONCLUSION

Three-phase HLV equilibria for simple and mixed hydrates of CO₂, N₂ and THF were determined at the broad ranges of temperature and pressure. Depending on the compositions of vapor phase, the equilibrium hydrate dissociation pressures were varied between two HLV curves of pure CO₂ and N₂. The dissociation pressures were largely shifted to higher temperature and lower pressure conditions by adding small amount of

THF. Accordingly, THF was confirmed to act as a hydrate promoter and extend hydrate stability region. This type of hydrate promoter can play an important role in changing high pressure condition to milder one, which provides a great advantage when applied to the real hydrate-based processes. In particular, the P - x diagram implies that the CO_2 can be recovered from a power-plant flue gas. The detailed researches related to this subject are now being carried out in our laboratory.

LIST OF SYMBOLS

a radius of the spherical core

P pressure [bar]

T temperature [K]

x mole fraction

Greek Letters

σ distance between the cores at zero potential energy

ε/κ depth of the intermolecular potential well

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Table 1. HLV equilibria of the CO₂+N₂+H₂O system

Loading composition (CO ₂)	Temperature (K)	Pressure (bar)
0.9659	274.95	15.65
	277.45	20.60
	280.25	29.00
	282.55	40.00
	283.55	51.15
0.7780	274.00	20.00
	276.15	26.00
	280.65	42.25
	283.45	64.50
	284.25	74.45
0.4815	273.75	31.95
	276.00	42.57
	279.00	58.67
	281.00	74.49
	282.00	89.75
0.1761	272.85	72.40
	274.05	81.20
	277.45	106.50
	278.65	117.48
	280.55	142.20
0.1159	274.25	110.20
	275.65	138.70
	277.60	181.00
	278.95	222.30
0.0663	273.95	140.85
	274.55	154.00
	277.00	206.80
	278.25	241.20

Table 2. HV equilibria of the CO₂+N₂+H₂O system measured at 274, 277 and 280 K

Temperature (K)	Pressure (bar)	Vapor phase (CO ₂)	Hydrate Phase (CO ₂)
274	13.94	1.0000	1.0000
	17.69	0.8205	0.9850
	23.54	0.5999	0.9517
	28.35	0.5048	0.9301
	35.60	0.3994	0.9001
	72.35	0.2057	0.5836
	112.00	0.1159	0.3426
	149.28	0.0498	0.1793
	179.26	0.0000	0.0000
277	19.53	1.0000	1.0000
	26.00	0.8491	0.9782
	33.77	0.5867	0.9455
	52.33	0.3899	0.8867
	119.80	0.1761	0.5400
	155.00	0.1159	0.3526
	191.74	0.0663	0.1928
	240.41	0.0000	0.0000
280	28.01	1.0000	1.0000
	36.00	0.8250	0.9765
	42.33	0.6999	0.9612
	50.68	0.5917	0.9432
	82.75	0.3924	0.8641
	149.74	0.2510	0.6400
	207.53	0.1709	0.4500
	266.90	0.0905	0.2217
	323.08	0.0000	0.0000

Table 3. HLV equilibria of the CO₂+N₂+THF+water system

Gas and THF concentration	Temperature (K)	Pressure (bar)
17 mol % CO ₂ , 1 mol % THF	274.95	4.40
	281.45	21.20
	287.85	60.70
	290.40	93.05
	282.15	129.05
17 mol % CO ₂ , 3 mol % THF	277.55	2.00
	281.85	11.40
	284.50	18.95
	289.65	47.00
	293.25	88.60
	295.15	128.20
70 mol % CO ₂ , 1 mol % THF	274.85	3.15
	282.45	17.70
	286.95	36.60
	290.85	75.70
	291.85	95.25
70 mol % CO ₂ , 3 mol % THF	279.55	3.80
	284.15	13.20
	289.35	32.00
	292.15	58.10
	295.45	90.86

Table 4. Optimized Kihara potential parameters of CO₂, N₂ and THF

	a (Å)	σ (Å)	ϵ/κ (Å)
CO ₂	0.720	2.8870	188.6
N ₂	0.3526	3.0298	125.07
THF	0.9643	3.2038	243.27

FIGURE CAPTIONS

Figure 1. Experimental apparatus for measuring hydrate phase equilibria

Figure 2. Hydrate phase equilibria for the CO_2+N_2 +water mixture measured at several composition ratios of CO_2 and N_2

Figure 3. P-x diagram of the CO_2+N_2 +water mixture measured at three temperatures of 274, 277 and 280 K

Figure 4. Hydrate phase equilibria for the CO_2+N_2 +THF+water mixture measured at 1 and 3 mol % of THF

Figure 1

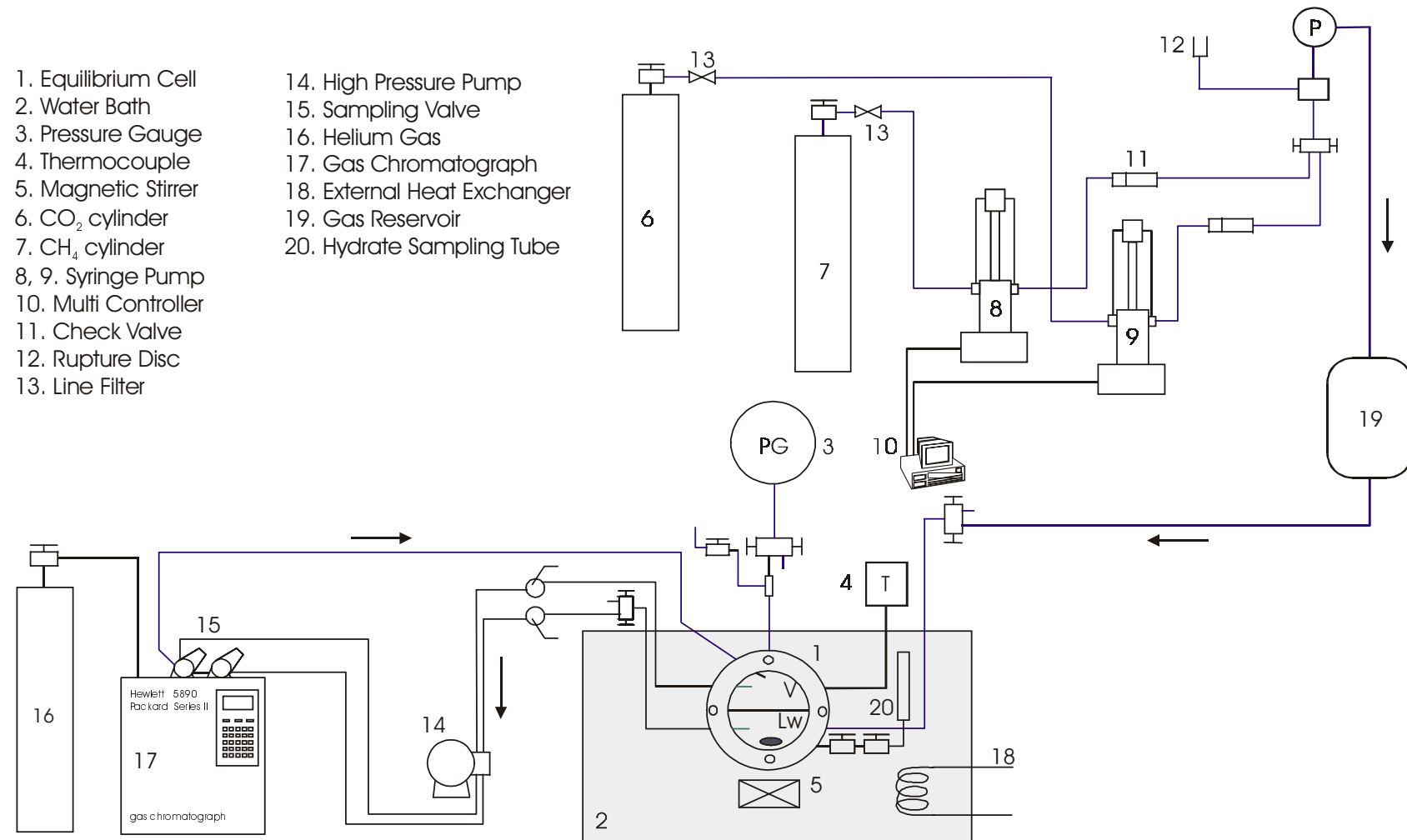


Figure 2

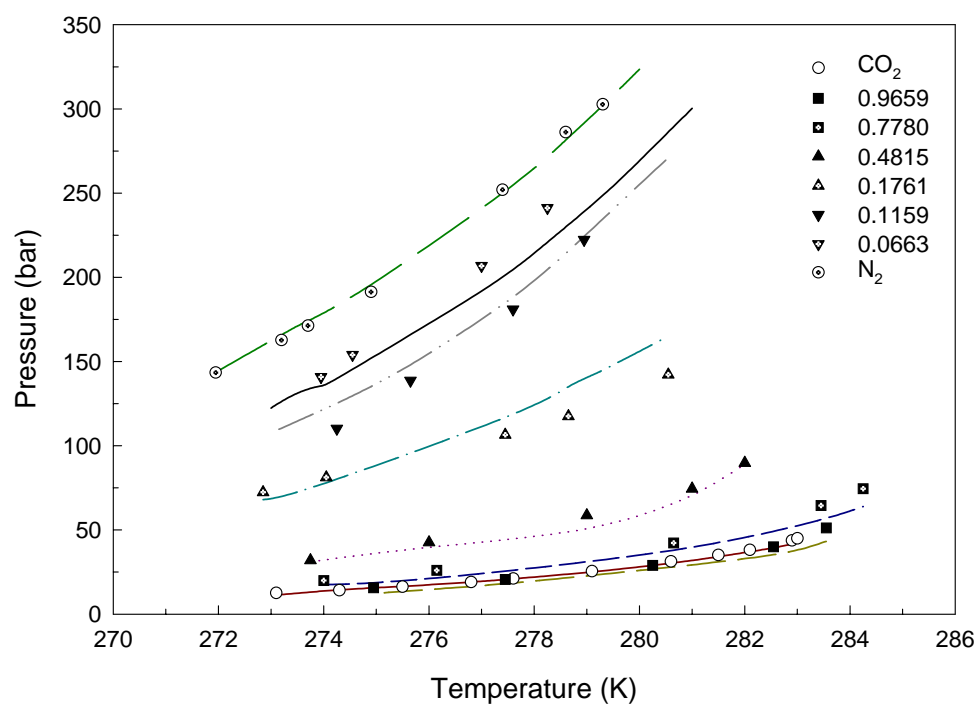


Figure 3

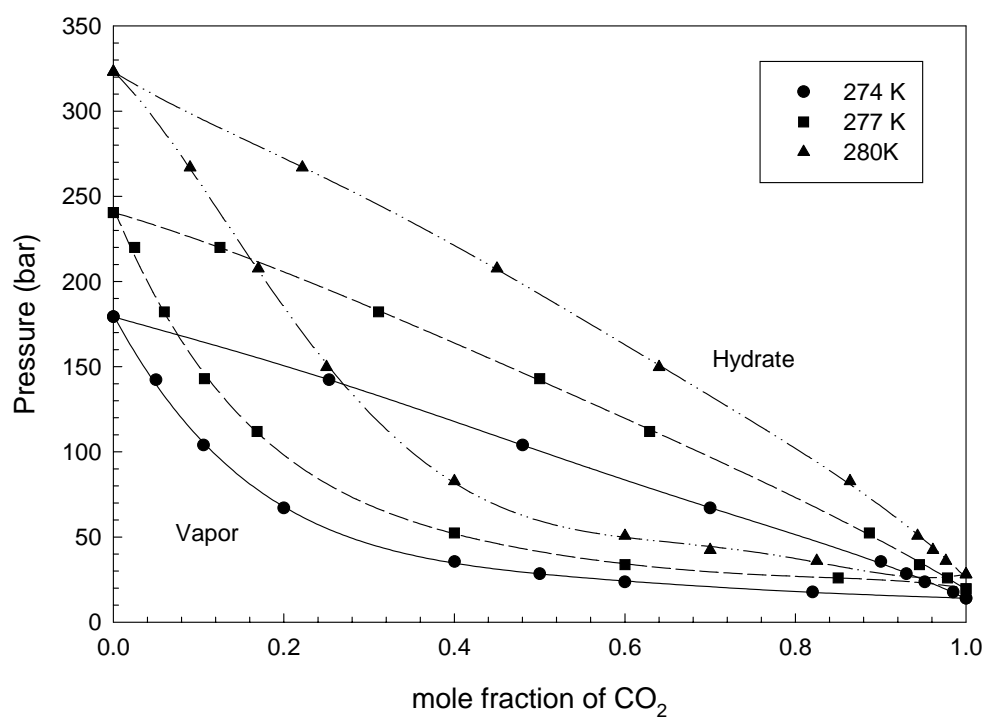


Figure 4

